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Comments on Chemical and Meteorological Effects and Their Relationship to the Problem of Environmental Control

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In recent years atmospheric chemistry has progressed quite rapidly in the recognition of important relationships among various naturally occurring and pollutant materials. An illustration of a set of such relationships is that amongst the molecules; oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, nitric acid, water, and methane, and the free radical species represented in general fashion by the formulas; HO_x, NO_x, CH_xO_y. This system, which we now understand in considerable detail, explains the chemistry of the stratosphere and how it may be affected by the emissions of oxides of nitrogen from high flying jet aircraft (including SST's). The same system of chemistry explains most of the important features of photochemical smog. In this latter case it is also necessary to consider reactions of various hydrocarbons other than methane. An important task of atmospheric scientists is to provide a proper means for determining how pollutant emissions interact with the "background" atmospheric chemical system which in turn is coupled to the dynamical system of atmospheric motions. Recent years have seen significant advancement in the techniques of numerical modeling wherein chemistry and atmospheric transport are represented. However much work remains to be done before these models will, if ever, be accepted by the scientific community as being a close representation of nature. Long before such acceptance, the models will be used as means to provide "engineering estimates" for the purposes of environmental control. The environmental administrator with a sophisticated model for predicting atmospheric pollution effects should not find reason for confidence and complacency in assuming the model results will lead to the only correct control strategy. Too often unverified models are used as the basis of environmental control. So while it is the rightful task of environmental scientists to provide models with proper verification (ultimately), it is the responsibility of those who use the models for environmental control to aid in the support of research and development of the models and, most emphatically, to support the acquisition of scientific data upon which to base the verification of the models.

I wish to illustrate, by means of an example of a current environmental problem, how models including the complexity of atmospheric chemical reactions and atmospheric transport phenomena can aid in environmental control. The system under consideration

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is that given above and the substance of concern is ozone, particularly at ground level. The federal air quality criteria state that ozone concentrations should not exceed 0.08 ppm for a 1-hr period more than 1 day/yr. Our knowledge of transport from the stratosphere to the troposphere, sketchy as it is, combined with data from various sites around the world leads us to suggest that as much as 0.04 ppm of ozone in the lower troposphere may originate in the stratosphere. Furthermore our knowledge of the chemical systems considered above coupled with some scattered observations indicates that normally less than 0.02 ppm of ozone would occur naturally from photochemical processes in the troposphere. However we know that there are natural sources of reactive hydrocarbons (namely terpenes from grasses, shrubs, and trees) which could conceivably cause ozone concentrations of the order of 0.05 ppm or more. There is also evidence that the air emanating from large cities may contain spent residues of photochemical smog and oxides of nitrogen which when mixed with ambient hydrocarbons and irradiated by sunlight could add to ozone concentrations. From these considerations it is seen that there might readily occur ozone concentrations in excess of 0.08 ppm in areas remote from cities. Indeed such concentrations have been observed in such places.

The question arises as to how to deal with the situation. Are there any means for control of these sources? Should the federal criteria be altered? In my view, we should base ultimate decisions on sound scientific knowledge. The tools for the job will consist of well-verified models which will include the chemistry and the atmospheric transport. At the present time we do not possess adequate meso-scale models (distances of 10–500 km) that are required to account for most of the phenomena discussed in the illustration above.

I would like briefly to mention another system where future control should be closely based on scientific knowledge not yet in hand. This system is that of stack plumes containing sulfur dioxide. It is well known that sulfur dioxide is oxidized in the atmosphere to form what is now referred to as "acid sulfate". As the plume mixes with the ambient atmosphere the oxidation proceeds at a rate that depends upon temperature, relative humidity, sulfur dioxide concentration, catalyst ion (such as Fe^{3+}, Mn^{2+}) concentrations in droplets, and ambient ammonia concentration. The detailed chemical mechanism of this system is unknown. We do know that the reactions are heterogeneous (reactions of gases with liquids and/or solids) in such a system and that they can be quite fast under certain conditions. To complicate matters even further it seems now (based on work by D. Davis at the University of Maryland) that in the presence of sunlight there may come important effects of photochemistry in producing not only sulfuric acid but also nitric acid and even ozone. To incorporate these two chemical systems along with the necessary micro- and meso-scale atmospheric dynamics to produce a model suitable for environmental control is truly a formidable task. However it does not seem insurmountable. Finally I point out that because long dwell time in the atmosphere favors the formation of acid sulfate, nitric acid, and ozone, the use of tall stacks will not favor reduction of these components.